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# Calculating frequency-dependent hyperpolarizabilities using time-dependent density functional theory

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An accurate determination of frequency-dependent molecular hyperpolarizabilities is at the same time of possible technological importance and theoretically challenging. For large molecules, Hartree–Fock theory was until recently the only available *ab initio* approach. However, correlation effects are usually very important for this property, which makes it desirable to have a computationally efficient approach in which those effects are (approximately) taken into account. We have recently shown that frequency-dependent hyperpolarizabilities can be efficiently obtained using time-dependent density functional theory. Here, we shall present the necessary theoretical framework and the details of our implementation in the Amsterdam Density Functional program. Special attention will be paid to the use of fit functions for the density and to numerical integration, which are typical of density functional codes. Numerical examples for He, CO, and para-nitroaniline are presented, as evidence for the correctness of the equations and the implementation. © 1998 American Institute of Physics. [S0021-9606(98)30247-0]

## I. INTRODUCTION

In recent years there has been a growing interest in non-linear optical (NLO) properties of molecules. NLO materials are important for optical-switching devices, applications in telecommunications, and for optical computing. Theory can play a leading role in finding suitable NLO materials if a reliable and efficient approach is available. In that case, theory can predict the NLO properties of large molecules with possibly large NLO responses. Density functional theory (DFT) has been shown to provide such an accurate and efficient technique for the prediction of energies and structures. It therefore seems appealing to use DFT for the prediction of NLO properties as well.

There are basically two different ways to calculate molecular properties which can be written in terms of energy derivatives, such as the polarizabilities and hyperpolarizabilities determining the linear and nonlinear optical response of a system. The first is to use finite difference techniques, where the energy is calculated for different values of, in our case, the electric field. The derivative of the energy is then obtained from a finite differentiation. This method is perfectly viable if one carefully chooses the strengths of the perturbations. It is a convenient method because it can be applied with any program capable of calculating the energy of the perturbed system, without extra programming effort.

There are also several drawbacks to this approach however. In the first place, it requires much human time (if the process has not been automated), because one has to check

the effect of varying the perturbation strengths carefully. Furthermore, one needs very well-converged energies in order to make reliable predictions, which makes the calculations much more time-consuming. Besides this, several calculations are needed in order to obtain one property. All these problems are amplified if one goes to higher (third or fourth) derivatives of the energy.

For these reasons the alternative, analytic, approach is often preferable. The desired properties are obtained from a single calculation by evaluating the derivatives of the energy analytically. The drawback is that a considerable programming effort may be required for certain properties, especially for the higher-order derivatives of the energy. However, once the programming has been done, the calculation of properties has become much more convenient and routine, as well as more accurate. One other important advantage of the analytical approach is that it gives access to time-dependent (or frequency-dependent) properties as well. There is no way to calculate properties which depend upon the frequency of the external field in the finite field (FF) approach.

In *ab initio* theoretical chemistry, the calculation of analytic derivatives has become routine for many time-dependent and time-independent properties, including higher-order properties. This is not yet the case in DFT, which has mainly been used for studying energies and geometries. The calculation of molecular response properties in DFT is relatively new, and is usually performed using FF techniques. This situation is however beginning to change.

Analytic formulations and computer implementations for such diverse second-order properties as NMR parameters,<sup>1–3</sup> ESR parameters,<sup>4–7</sup> magnetizabilities,<sup>8</sup> and polarizabilities<sup>9</sup> are now available. The results are encouraging in that they are usually superior to those obtained at the Hartree–Fock (HF) level.

Higher-order properties, such as hyperpolarizabilities and Raman scattering intensities and depolarization ratios, are usually treated by finite difference techniques. In this work, on the contrary, the analytical approach will be used for calculating frequency-dependent hyperpolarizabilities within DFT. The first application of our implementation, to the C<sub>60</sub> molecule, has recently been published elsewhere,<sup>10</sup> but contains only a rough outline of the underlying theory. In the present work, which will be of a rather technical nature, we shall describe our implementation in the Amsterdam Density Functional (ADF) program<sup>11–14</sup> in more detail. As there are many analogies to the calculation of frequency-dependent hyperpolarizabilities in time-dependent Hartree–Fock (TDHF) theory, which has become routine by now, those parts of the derivation and implementation which are typical of time-dependent DFT (TDDFT) will be emphasized.

In particular, we will derive the starting equation of this paper (a variation on the so-called time-dependent Kohn–Sham (KS) equations of DFT), present equations for functional derivatives of the time-dependent exchange–correlation (xc) potential, which replaces the Hartree–Fock exchange operator, and present concise final DFT results, using the (2n + 1)-rule, for the first hyperpolarizability tensor  $\beta_{abc}(-\omega_\sigma; \omega_b, \omega_c)$  for several important NLO properties.

In a more technical sense, we will discuss the influence of using so-called auxiliary basis sets for fitting the density, which are used in most modern DFT codes. Accuracy issues related to numerical integrations, which are needed in DFT because integrals involving the complicated xc potential cannot be calculated analytically, will also be discussed. It is shown that the errors introduced through these approximations can be kept under control.

Our implementation for the calculation of frequency-dependent hyperpolarizabilities presents the first analytic implementation of a third-order time-dependent property in DFT, which is applicable to general molecules. The efficiency of the resulting implementation is similar to that of an ordinary energy calculation in DFT, namely  $N^3$ . This, in combination with the use of symmetry, and, in future refinements to the code, of linear scaling techniques,<sup>14</sup> as well as a fully vectorized and parallelized code, will enable one to treat large molecules (more than 100 atoms) at a level of theory which usually supersedes Hartree–Fock. Here, only numerical examples on He, CO, and para-nitroaniline will be presented in order to document the technical accuracy of the implementation. A comparative study on frequency-dependent hyperpolarizabilities of a set of small molecules, in which the performance of various xc potentials is compared to that of (correlated) *ab initio* methods, is reported in another paper.<sup>15</sup>

## II. THE BASIC EQUATIONS

In TDHF, the starting point for the calculation of NLO properties is given by<sup>16–18</sup>

$$FC - i \frac{\partial}{\partial t} SC = SC\varepsilon, \quad (1)$$

where  $F$ ,  $C$ ,  $S$ , and  $\varepsilon$  are the Fock, coefficient, overlap and Lagrangian multiplier matrices, to be specified in detail below. This equation is derived from Frenkel's variational principle<sup>19–22</sup> for the total wave function  $\Psi$ , to which the HF wave function is an approximation. It would be desirable to start the DFT treatment of these properties from a similar equation, because many of the well-developed TDHF techniques can be used in that case. However, the DFT wave function, which is the Slater determinant of the KS orbitals, is not equal to the exact wave function, which prohibits the use of Frenkel's principle.

Instead, in TDDFT one searches for a stationary point of the action integral  $\mathcal{A}$ ,

$$\mathcal{A} = \int_{t_0}^{t_1} dt \langle \Psi(t) | i \frac{\partial}{\partial t} - \hat{H}(t) | \Psi(t) \rangle, \quad (2)$$

where  $\Psi$  is the total wave function of the system. In view of the correspondence between the time-dependent densities and wave functions, this action functional can be regarded as a density functional  $\mathcal{A}[\rho]$ , which must have a stationary point at the exact time-dependent density,<sup>23</sup> which is the central quantity in TDDFT. This exact density can be found from the Euler–Lagrange equation  $\delta \mathcal{A}[\rho] / \delta \rho(\mathbf{r}, t) = 0$ . The action functional  $A$  is given in terms of time-dependent single-particle orbitals  $\{\phi_j(\mathbf{r}, t)\}$  by<sup>24,25</sup>

$$\begin{aligned} A[\{\phi_j\}] = & \sum_j^N \int_{-\infty}^{t_1} dt \int d^3\mathbf{r} \phi_j^*(\mathbf{r}, t) \left( i \frac{\partial}{\partial t} + \frac{\nabla^2}{2} \right) \\ & \times \phi_j(\mathbf{r}, t) - \int_{-\infty}^{t_1} dt \int d^3\mathbf{r} \rho(\mathbf{r}, t) v_{\text{ext}}(\mathbf{r}, t) \\ & - \frac{1}{2} \int_{-\infty}^{t_1} dt \int d^3\mathbf{r} \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}, t) \rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} \\ & - A_{\text{xc}}[\{\phi_j\}], \end{aligned} \quad (3)$$

where all unknown many-body terms are hidden in the xc-part of the action functional  $A_{\text{xc}}$ , of which the functional derivative with respect to the time-dependent density is called the time-dependent xc-potential  $v_{\text{xc}}(\mathbf{r}, t)$ . If we explicitly demand the orbitals to remain orthonormal at all times, by adding to the action functional  $A$  the constraint term  $A^{\text{constraint}}$ , involving Lagrangian multipliers  $\varepsilon_{ij}$ ,

$$A^{\text{constraint}} = \sum_{ij} \varepsilon_{ij}(t) \left( \delta_{ij} - \int d^3\mathbf{r} \phi_i^*(\mathbf{r}, t) \phi_j(\mathbf{r}, t) \right), \quad (4)$$

and we demand the resulting total action functional to be stationary with respect to orbital variations  $\partial A / \partial \phi_k^* = 0$ , we obtain a general form of the time-dependent KS equations,<sup>26</sup>

$$\sum_j \varepsilon_{ij}(t) \phi_j(\mathbf{r}, t) + i \frac{\partial}{\partial t} \phi_i(\mathbf{r}, t) = \left[ -\frac{\nabla^2}{2} + v_s(\mathbf{r}, t) \right] \phi_i(\mathbf{r}, t) \equiv F_s \phi_i(\mathbf{r}, t), \quad (5)$$

where  $v_s(\mathbf{r}, t)$  is the time-dependent KS potential, and where the time-dependent density  $\rho(\mathbf{r}, t)$  is obtained from the squares of the occupied orbitals

$$\rho(\mathbf{r}, t) = \sum_i^{\text{occ}} |\phi_i(\mathbf{r}, t)|^2. \quad (6)$$

If the orbitals  $\phi_i$  of Eq. (5) are expanded in a fixed, time-independent basis set of AOs  $\{\chi_\mu\}$ ,

$$\phi_i(\mathbf{r}, t) = \sum_\mu \chi_\mu(\mathbf{r}) C_{\mu i}(t), \quad (7)$$

where the time-dependence of  $\phi_i$  is completely determined by the coefficient matrix  $C$ , we obtain the desired matrix form of the time-dependent KS equations, which will form the starting point of the perturbative expansion,

$$F_s C - i \frac{\partial}{\partial t} S C = S C \varepsilon, \quad (8)$$

where  $F_s$  is now the AO matrix of the operator defined in Eq. (5), and  $S$  is the overlap matrix of the AOs [ $S_{\mu\nu} = \int d\mathbf{r} \chi_\mu^*(\mathbf{r}) \chi_\nu(\mathbf{r})$ ]. The matrix equation for the orthonormality constraint reads

$$\frac{\partial}{\partial t} (C^\dagger S C) = 0 \quad (9)$$

[and  $(C^\dagger S C) = 1$  at  $t \rightarrow -\infty$ ], and the density matrix  $D$  is known from the coefficient matrix  $C$  and the occupation number matrix  $n$ ,

$$D = C n C^\dagger. \quad (10)$$

Although all equations can be extended to the spin-unrestricted case,<sup>27</sup> we will be dealing with closed-shell systems only in this paper, in which case the matrix  $n$  is diagonal with components either equal to 2 (occupied KS orbitals) or 0 (virtual KS orbitals).

Different choices for the Lagrangian multipliers  $\varepsilon_{ij}(t)$  are allowed. The “canonical” form of the time-dependent KS equations is obtained from the choice  $\varepsilon_{ij}(t) \equiv 0$ , which has implicitly been made by Runge and Gross<sup>23</sup> in their derivation of the time-dependent KS equations. There is no objection to that particular choice because the Hermiticity of the Hamiltonian assures the orthonormality of the orbitals in that case. However, the choice  $\varepsilon_{ij}(t) \equiv 0$  is not the most suitable one for our present purpose of finding higher-order perturbative solutions to the time-dependent KS equations, as was already discussed by Langhoff, Epstein, and Karplus in their review article on time-dependent perturbation theory.<sup>21</sup> It would lead to orbitals which vary rapidly in time, and cause so-called normalization and secular terms<sup>21</sup> to occur. If these terms are not dealt with properly, which is a technically cumbersome task, they may lead to unphysical divergences in the equations. These troublesome terms can

be factored from the equations for all orders by making suitable choices for the Lagrangian multipliers, as will be done here. In this manner, many problems are automatically circumvented and the proper passage to the time-independent equations for static perturbations is guaranteed. This can be done, anticipating the expansion of all matrices in different orders of the external perturbation, by choosing a diagonal time-independent zeroth-order  $\varepsilon$ -matrix, resulting in the ordinary canonical KS equations of ground-state DFT for the zeroth-order equation,

$$F_s^{(0)} C^{(0)} = S^{(0)} C^{(0)} \varepsilon^{(0)}, \quad (11)$$

where  $\varepsilon^{(0)}$  is a diagonal matrix containing the KS orbital energies. One has a freedom of choice for the Lagrangian multiplier matrix in each order of the perturbation<sup>21,28</sup> (although it necessarily is block-diagonal and Hermitian<sup>20</sup>). In case the Lagrangian matrix is chosen diagonal in all orders, the corresponding time-dependent orbitals  $\phi_i^{\text{diag}}$  are easily seen [from Eq. (5)] to be identical to the canonical KS orbitals  $\phi_i^{\text{can}}$  (which correspond to  $\varepsilon \equiv 0$ ) up to a purely imaginary time-dependent phase factor,

$$\phi_i^{\text{diag}} = \phi_i^{\text{can}} \times \exp \left[ i \int_{-\infty}^t \varepsilon_i(t') dt' \right]. \quad (12)$$

In fact, Eq. (8) can be obtained by inserting the definition of the “diagonal-gauge” orbitals in the canonical time-dependent KS equations. Finally, we remark that we do not use a diagonal  $\varepsilon$ -matrix, because there are technical advantages,<sup>17,28</sup> to be discussed below, in choosing  $\varepsilon$  nondiagonal for the higher-order equations.

### III. EXPANSION OF BASIC EQUATIONS

We consider a system in external electric fields  $\mathbf{E}^a(\mathbf{r}, t)$ ,  $\mathbf{E}^b(\mathbf{r}, t)$ , ... consisting of a monochromatic and a static part,

$$\mathbf{E}^a(\mathbf{r}, t) = \mathbf{E}^a(\mathbf{r}) \times [1 + e^{i\omega_a t} + e^{-i\omega_a t}], \quad (13)$$

labeled with the Cartesian directions  $a, b, \dots$  equal to  $x, y$ , or  $z$ . Although our approach can be used for general frequencies  $\omega_a, \omega_b, \dots$ , the implementation is at present restricted to frequencies which are either equal to 0 or to some common frequency  $\omega$ . Most of the important NLO phenomena, such as second harmonic generation (SHG), and many others, arise from interactions of multiple monochromatic and static fields and can consequently be described with the equations in this work.

In the dipole approximation, the external perturbation term  $\mathcal{H}'$  in the KS Hamiltonian becomes

$$\mathcal{H}' = \boldsymbol{\mu} \cdot \mathbf{E}(\mathbf{r}, t), \quad (14)$$

where  $\boldsymbol{\mu}$  is the dipole moment operator of the electrons. The equations presented in this section until now, are identical to those used in TDHF theory.<sup>16,18,17</sup> The difference enters through the Fock or KS matrix. In TDHF theory it is given by<sup>16,18,17</sup>

$$F = h + D \times (2J - K). \quad (15)$$

Here  $h$  is the one-electron integral matrix, containing the kinetic energy and the Coulomb field of the nuclei, as well as the external electric field of Eq. (14).  $D$  is once again the density matrix, and  $J$  and  $K$  are the four-index Coulomb and exchange supermatrices. We have used a notation which slightly differs from the one used in earlier work<sup>17</sup> in order to make the multiplication of the two-index and four-index matrices more explicit. The KS matrix  $F_s$  is obtained by the substitution

$$D \times (K) \rightarrow v_{xc}, \quad (16)$$

where  $v_{xc}$  is the matrix form of the (time-dependent) xc potential. Contrary to its HF counterpart  $K$ , the matrix  $v_{xc}$  is a two-index matrix, obtained from the local xc potential  $v_{xc}$ ,

$$[v_{xc}]_{\kappa\lambda} = \int d\mathbf{r} \chi_{\kappa}(\mathbf{r}) v_{xc}(\mathbf{r}, t) \chi_{\lambda}(\mathbf{r}). \quad (17)$$

In this equation and the following ones, complex conjugate signs have been left out, as we are assuming real AOs and KS orbitals. Obviously, the fact that the KS xc potential is local, in contrast to the nonlocal exchange potential in HF theory, simplifies the DFT response calculations. On the other hand, because the approximations for  $v_{xc}$  are not of the same simplicity as the HF exchange potential, the integrals in which  $v_{xc}$  or related quantities occur cannot be calculated analytically and have to be obtained by numerical integration. Another important difference between the HF exchange potential and the KS xc potential is that the latter is a non-linear functional of the density, while the exchange matrix  $D \times (K)$  has a linear dependence. It will be shown in the rest of this work that, for this reason, the DFT equations for the various NLO properties contain certain extra terms which are not present in the TDHF equations, as presented for example by Karna and Dupuis.<sup>17</sup>

The goal is to start from the equations given above and to end up with equations for the various linear and nonlinear polarizabilities (hyperpolarizabilities), which can be defined through an expansion of the dipole moment into different orders of the external fields,

$$\begin{aligned} \mu_a = & \mu_a(E^b = E^c = E^d = \dots = 0) + \sum_b \alpha_{ab} E^b \\ & + \frac{1}{2!} \sum_{bc} \beta_{abc} E^b E^c + \frac{1}{3!} \sum_{bcd} \gamma_{abcd} E^b E^c E^d. \end{aligned} \quad (18)$$

The time dependence of the dipole moment can be written out explicitly,<sup>29</sup> leading to the various frequency-dependent hyperpolarizability tensors. These tensors can be obtained from the trace of the dipole moment matrix  $H^a$  and the  $n$ th order density matrix  $D^{(n)}$  (where  $n=1$  for the linear polarizability  $\alpha$ ,  $n=2$  for the first hyperpolarizability tensor  $\beta$ , and so on), induced by electric fields in directions  $b, c, \dots$ , of frequency  $\omega_b, \omega_c, \dots$ ,

$$\begin{aligned} \alpha_{ab}(-\omega_{\sigma}; \omega_b) &= -\text{Tr} [H^a D^b(\omega_b)], \\ \beta_{abc}(-\omega_{\sigma}; \omega_b, \omega_c) &= -\text{Tr} [H^a D^{bc}(\omega_b, \omega_c)], \\ \gamma_{abcd}(-\omega_{\sigma}; \omega_b, \omega_c, \omega_d) &= -\text{Tr} [H^a D^{bcd}(\omega_b, \omega_c, \omega_d)]. \end{aligned} \quad (19)$$

Here, the usual convention is adopted that  $\omega_b, \omega_c$  and  $\omega_d$  refer to the frequencies of the external fields, while  $\omega_{\sigma}$  is equal to the sum of these frequencies:  $\omega_{\sigma} = \omega_b + \omega_c + \dots$ . As stated before, we will treat only those cases in which the frequencies of the external electric fields are either equal to zero or equal to  $\omega$ . This gives access to such important properties as second harmonic generation (SHG) [ $\beta(-2\omega; \omega, \omega)$ ], third harmonic generation (THG) [ $\gamma(-3\omega; \omega, \omega, \omega)$ ], and the electro-optical Kerr effect (EOKE) [ $\gamma(-\omega; \omega, 0, 0)$ ], as well as many others.<sup>16,17</sup> Some of these properties can be obtained by a combination of analytical and finite difference techniques. For example, all components of the  $\gamma$ -tensor governing the EOKE can be obtained from analytical time-dependent calculations on the electro-optical Pockels effect (EOPE) tensor  $\beta(-\omega; \omega, 0)$  in various small electric fields in various directions, by the relation,

$$\gamma_{abcd}(-\omega; \omega, 0, 0) = \lim_{E^d \rightarrow 0} \frac{\beta_{abc}(-\omega; \omega, 0)|_{E=E^d}}{E^d}. \quad (20)$$

This means that an analytic implementation for arbitrary  $\beta$ -tensors gives access to certain frequency-dependent  $\gamma$ -tensors as well, through finite difference techniques. This was, for example, used in our first application of the present techniques, on the frequency-dependent hyperpolarizability  $\gamma$  of the  $C_{60}$  molecule.<sup>10</sup>

As in the TDHF case, the main technical difficulty is to rewrite Eq. (19) in such a way that the so-called  $(2n+1)$ -theorem is exploited. This theorem states that if the wave function is known up to order  $n$ , the energy can be obtained up to order  $2n+1$ . In the present case, it means that the static first hyperpolarizability tensor  $\beta$ , which corresponds to the third-order term of the energy in a Taylor expansion with respect to an electric field, can be obtained from the knowledge of first-order quantities in the field only, implying that the so-called second-order perturbed equations do not have to be solved. In other words, one can rewrite Eq. (19) for  $\beta$  in such a way that the second-order density matrix is not needed. Both Karna and Dupuis<sup>17</sup> and Rice *et al.*<sup>18</sup> have explicitly shown for the TDHF case, that the  $(2n+1)$ -theorem can be used for the frequency-dependent hyperpolarizabilities also. Karna and Dupuis have given explicit expressions for all major NLO properties up to third-order ( $\gamma$ ). In this work, we follow the paper by Karna and Dupuis, and our aim is to indicate what differences with respect to their results appear in the DFT case. From these differences, one obtains the explicit expressions for all those properties in the DFT case as well. Some comments will be made about the efficient implementation of these equations.

In the DFT case, methods for calculating (frequency-dependent)  $\beta$  and  $\gamma$ 's have been given by Zangwill<sup>30</sup> and by Senatore and Subbaswamy<sup>31,32</sup> for the atomic case, using spherical symmetry. Apart from this restriction, they do not use the  $(2n+1)$ -theorem. This implies that an implementation of their equations will necessarily be less efficient than a calculation along the lines of this paper. For static first hyperpolarizabilities  $\beta$ , Colwell *et al.*<sup>33,34</sup> have presented equations which can be used in the molecular case and which do

make use of the  $(2n+1)$ -theorem. Both for the case where the local density approximation (LDA) is used for the xc potential and its derivatives<sup>33</sup> and for the case where a generalized gradient approximation (GGA) is used,<sup>34</sup> they provide expressions for  $\beta_{abc}(0;0,0)$ , with applications to  $\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{F}$  and  $\text{CH}_3\text{CN}$ . Their work is similar in nature to the work of Rice *et al.*<sup>18</sup> This is also true for their paper on frequency-dependent polarizabilities,<sup>35</sup> using the current-density functional theory approach. By following in the track of Rice *et al.*, their approach could be extended to the frequency-dependent hyperpolarizability case. However, as we are mainly interested in electric properties, the consideration of magnetic fields, as in current-density functional theory, is unnecessary. In any case, the effect of the current-density has been shown to be very small.<sup>36</sup>

The way to proceed from here is to expand the equations presented above in different orders of the electric field. After that, first-order and higher-order equations are obtained in which quantities with the same frequency dependence are taken together. The solution to these equations will yield the first and higher-order density matrices which are needed for the calculation of the frequency-dependent (hyper)polarizabilities in Eq. (19). The expansion in different orders of the electric field proceeds identically for all matrices which are involved. As an example, we give the expansion of the density matrix  $D$ ,<sup>17</sup>

$$D = D^{(0)} + \sum_a E^a D^a + \frac{1}{2!} \sum_{a,b} E^a E^b D^{ab} + \frac{1}{3!} \sum_{a,b,c} E^a E^b E^c D^{abc} + \dots \quad (21)$$

By combining all terms of a certain order in one symbol, irrespective of their frequency dependencies, we have adopted the same shorthand notation as Karna and Dupuis, which also implies that, here and in the following, the number of indices  $a, b, \dots$  indicates the order of the associated matrix. For example, the symbol  $D^{ab}$  is short for

$$D^{ab} = e^{+2i\omega t} D^{ab}(\omega, \omega) + e^{+i\omega t} [D^{ab}(0, \omega) + D^{ab}(\omega, 0)] + D^{ab}(\omega, -\omega) + D^{ab}(-\omega, \omega) + D^{ab}(0, 0) + e^{-i\omega t} [D^{ab}(0, -\omega) + D^{ab}(-\omega, 0)] + e^{-2i\omega t} D^{ab}(-\omega, -\omega). \quad (22)$$

The matrices  $F$ ,  $C$ ,  $S$ , and  $\varepsilon$  can be expanded in a similar fashion.<sup>17</sup> However, as we are using a fixed AO basis set, the overlap matrix  $S$  is independent of the field ( $S = S^{(0)}$ ), resulting in vanishing terms above zeroth-order. The same holds for the Coulomb supermatrix  $J$  and the Hartree-Fock exchange matrix  $K$ , but not for its DFT equivalent  $v_{\text{xc}}$ . As the most important difference between the TDHF equations and the time-dependent DFT equations arises from this difference between the HF exchange potential and the xc potential in DFT, we will show in the next section how the xc potential is expanded in different orders of the electric field.

#### IV. EXPANSION OF XC POTENTIAL

In this section, we show what a functional Taylor expansion of the time-dependent xc potential with respect to external electric perturbations looks like. We use the compact four-vector notation  $\mathbf{x} = (\mathbf{r}, t)$  as in Ref. 25 and start from the formula for a functional Taylor expansion<sup>37</sup> of a functional  $v_{\text{xc}}$  in the space-time point  $\mathbf{x}$ , with a functional dependence on the total external potential  $v_{\text{ext}}$  (which includes the interaction with the nuclei, etcetera). If this external potential is slightly perturbed by the electric field  $E$ , we have

$$v_{\text{xc}}[v_{\text{ext}} + \mu \cdot E](\mathbf{x}) = v_{\text{xc}}[v_{\text{ext}}](\mathbf{x}) + \int \frac{\delta v_{\text{xc}}(\mathbf{x})}{\delta v_{\text{ext}}(\mathbf{y})} \Big|_{E=0} \times \mu \cdot E(\mathbf{y}) d\mathbf{y} + \frac{1}{2!} \int \int \frac{\delta^2 v_{\text{xc}}(\mathbf{x})}{\delta v_{\text{ext}}(\mathbf{y}) \delta v_{\text{ext}}(\mathbf{y}')} \Big|_{E=0} \times \mu \cdot E(\mathbf{y}) \mu \cdot E(\mathbf{y}') d\mathbf{y} d\mathbf{y}' + \dots, \quad (23)$$

where all functional derivatives are to be evaluated at the unperturbed external potential ( $E=0$ ). Splitting the electric perturbation in its Cartesian components  $\mu_a E^a, \mu_b E^b, \dots$  as in Eq. (13), this becomes

$$v_{\text{xc}} \left[ v_{\text{ext}} + \sum_a \mu_a E^a \right](\mathbf{x}) = v_{\text{xc}}[v_{\text{ext}}](\mathbf{x}) + \sum_a \int \frac{\delta v_{\text{xc}}(\mathbf{x})}{\delta v_{\text{ext}}(\mathbf{y})} \Big|_{\rho=\rho^{(0)}} \mu_a E^a(\mathbf{y}) d\mathbf{y} + \frac{1}{2!} \sum_a \sum_b \int \int \frac{\delta^2 v_{\text{xc}}(\mathbf{x})}{\delta v_{\text{ext}}(\mathbf{y}) \delta v_{\text{ext}}(\mathbf{y}')} \Big|_{\rho=\rho^{(0)}} \times \mu_a E^a(\mathbf{y}) \mu_b E^b(\mathbf{y}') d\mathbf{y} d\mathbf{y}' + \dots, \quad (24)$$

where the derivatives are evaluated at the converged SCF density  $\rho^{(0)}$  (equivalent to  $E=0$ ). Although all results can be generalized to higher order, we will restrict ourselves to two fields here, as this is sufficient for our present purposes.

Instead of the functional derivatives with respect to external perturbations in Eq. (24), we require derivatives with respect to perturbed densities. Similar derivatives have been considered in Ref. 25, and by direct analogy to Eq. (179) in Sec. 5.2 of that work, we get

$$\frac{\delta^2 v_{\text{xc}}(\mathbf{x})}{\delta v_{\text{ext}}(\mathbf{y}) \delta v_{\text{ext}}(\mathbf{y}')} = \int d\mathbf{z} \int d\mathbf{z}' \frac{\delta^2 v_{\text{xc}}(\mathbf{x})}{\delta \rho(\mathbf{z}') \delta \rho(\mathbf{z})} \frac{\delta \rho(\mathbf{z}')}{\delta v_{\text{ext}}(\mathbf{y}')} \times \frac{\delta \rho(\mathbf{z})}{\delta v_{\text{ext}}(\mathbf{y}')} + \int d\mathbf{z} \frac{\delta v_{\text{xc}}(\mathbf{x})}{\delta \rho(\mathbf{z})} \times \frac{\delta^2 \rho(\mathbf{z})}{\delta v_{\text{ext}}(\mathbf{y}) \delta v_{\text{ext}}(\mathbf{y}')} \quad (25)$$

with a similar expression for the first functional derivative. Here, all functional derivatives are again to be evaluated at  $\rho = \rho^{(0)}$ . We employ the usual notation<sup>25</sup> for the functional

derivatives of the time-dependent xc potential with respect to the time-dependent density (or densities). These functional derivatives  $f_{xc}$  and  $g_{xc}$  are the so-called xc kernels of TD-DFT,

$$f_{xc}(\mathbf{z}, \mathbf{z}') \equiv \left. \frac{\delta v_{xc}(\mathbf{z})}{\delta \rho(\mathbf{z}')} \right|_{\rho=\rho^{(0)}}, \quad (26)$$

$$g_{xc}(\mathbf{z}, \mathbf{z}', \mathbf{z}'') \equiv \left. \frac{\delta^2 v_{xc}(\mathbf{z})}{\delta \rho(\mathbf{z}') \delta \rho(\mathbf{z}'')} \right|_{\rho=\rho^{(0)}}.$$

The functional derivatives  $\delta \rho(\mathbf{x}) / \delta v_{ext}(\mathbf{y})$  and  $\delta^2 \rho(\mathbf{x}) / \delta v_{ext}(\mathbf{y}) \delta v_{ext}(\mathbf{y}')$  are in fact the exact first- and second-order response functions, which relate the perturbations  $\mu_a E^a, \mu_b E^b, \dots$  to the perturbed first- and second-order densities  $\rho^a$  and  $\rho^{ab}$ ,

$$\rho^a(\mathbf{x}) = \int d\mathbf{y} \frac{\delta \rho(\mathbf{x})}{\delta v_{ext}(\mathbf{y})} \mu_a E^a(\mathbf{y}), \quad (27)$$

$$\rho^{ab}(\mathbf{x}) = \int d\mathbf{y} \int d\mathbf{y}' \frac{\delta^2 \rho(\mathbf{x})}{\delta v_{ext}(\mathbf{y}) \delta v_{ext}(\mathbf{y}')} \times \mu_a E^a(\mathbf{y}) \mu_b E^b(\mathbf{y}').$$

Combining the notation of the xc kernels with these identities, and substituting everything in Eq. (24) leads to

$$\begin{aligned} v_{xc}(\mathbf{x}) &= v_{xc}^{(0)}(\mathbf{x}) + \sum_a \int d\mathbf{z} f_{xc}(\mathbf{x}, \mathbf{z}) \rho^a(\mathbf{z}) \\ &+ \frac{1}{2!} \sum_{a,b} \left[ \int d\mathbf{z} \int d\mathbf{z}' g_{xc}(\mathbf{x}, \mathbf{z}', \mathbf{z}) \rho^a(\mathbf{z}') \rho^b(\mathbf{z}) \right. \\ &\left. + \int d\mathbf{z} f_{xc}(\mathbf{x}, \mathbf{z}) \rho^{ab}(\mathbf{z}) \right] + \dots \end{aligned} \quad (28)$$

We want to write this equation in the same shorthand notation as was used for the density matrix in Eqs. (21) and (22), using the fact that the  $n$ th order density  $\rho^{ab \dots n}$  is known in terms of the associated density matrix,

$$\rho^{ab \dots n}(\mathbf{r}, t) = \sum_{\mu\nu} [D^{ab \dots n}(t)]_{\mu\nu} \chi_\mu(\mathbf{r}) \chi_\nu(\mathbf{r}). \quad (29)$$

If we furthermore use that only the differences  $t - t'$ ,  $t - t''$  between the time variables  $t$ ,  $t'$ , and  $t''$ , associated with, respectively,  $x$ ,  $z$ , and  $z'$ , are of importance, we arrive after some algebra at the final result for this section,

$$[v_{xc}^a(\omega_a)]_{\kappa\lambda} = \sum_{\mu\nu} [f_{xc}(\omega_a)]_{\kappa\lambda\mu\nu} [D^a(\omega_a)]_{\mu\nu}, \quad (30)$$

$$\begin{aligned} [v_{xc}^{ab}(\omega_a, \omega_b)]_{\kappa\lambda} &= \sum_{\mu\nu} [f_{xc}(\omega_a + \omega_b)]_{\kappa\lambda\mu\nu} [D^{ab}(\omega_a, \omega_b)]_{\mu\nu} \\ &+ \sum_{\mu\nu} \sum_{\sigma\tau} [g_{xc}(\omega_a, \omega_b)]_{\kappa\lambda\mu\nu\sigma\tau} \\ &\times [D^a(\omega_a)]_{\mu\nu} [D^b(\omega_b)]_{\sigma\tau}, \end{aligned}$$

where we have adopted the following notation for the matrix elements of the Fourier-transformed xc kernels:

$$\begin{aligned} [f_{xc}(\omega_a)]_{\kappa\lambda\mu\nu} &= \int d\mathbf{r} \int d\mathbf{r}' \chi_\kappa(\mathbf{r}) \chi_\lambda(\mathbf{r}) \\ &\times f_{xc}(\mathbf{r}, \mathbf{r}', \omega_a) \chi_\mu(\mathbf{r}') \chi_\nu(\mathbf{r}') \end{aligned} \quad (31)$$

$$\begin{aligned} [g_{xc}(\omega_a, \omega_b)]_{\kappa\lambda\mu\nu\sigma\tau} &= \int d\mathbf{r} \int d\mathbf{r}' \int d\mathbf{r}'' \chi_\kappa(\mathbf{r}) \chi_\lambda(\mathbf{r}) \\ &\times g_{xc}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_a, \omega_b) \chi_\mu(\mathbf{r}') \\ &\times \chi_\nu(\mathbf{r}') \chi_\sigma(\mathbf{r}'') \chi_\tau(\mathbf{r}''). \end{aligned}$$

We emphasize already at this point that these matrix elements are never actually evaluated in practical calculations, as this would be very time-consuming. Equation (30) for  $v_{xc}^{(2)}$  is a generalization of Eq. (79) in Ref. 38 for the static case, which reads

$$v_{xc}^{bc} = v'_{xc} \rho^{bc} + v''_{xc} \rho^b \rho^c, \quad (32)$$

and which can be regarded as an application of the ordinary chain rule for differentiation. The frequency-dependent extension of the related third-order expression

$$v_{xc}^{abc} = v'''_{xc} \rho^a \rho^b \rho^c + v''_{xc} (\rho^{ab} \rho^c + \rho^{ac} \rho^b + \rho^{bc} \rho^a) + v'_{xc} \rho^{abc} \quad (33)$$

is required for such properties as the THG.

## V. EXPRESSIONS FOR THE HIGHER-ORDER KOHN-SHAM MATRICES IN DFT

Using the results of the previous section, and the same expansion of the KS matrix as was given for the density matrix in Eqs. (21) and (22), we can derive the DFT expression for the higher-order KS matrices. The zeroth-order KS matrix is the one used in ordinary (time-independent) DFT,

$$F_s^{(0)} = h^{(0)} + D^{(0)} \times (2J) + v_{xc}^{(0)}, \quad (34)$$

where  $h^{(0)}$  contains the external potential terms which are of zero order in the external field: the kinetic energy and nuclear Coulomb field. The Coulomb supermatrix  $J$  is independent of the field, resulting in a Coulomb term in the  $n$ th

order KS matrix  $F_s^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n)$  of the form  $D^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n) \times (2J)$ . Only in the first-order KS matrices, the external perturbation  $H^a$  appears,

$$F_s^a(\omega_a) = H^a + D^a(\omega_a) \times (2J) + v_{xc}^a(\omega_a), \quad (35)$$

$$F_s^a(0) = H^a + D^a(0) \times (2J) + v_{xc}^a(0).$$

Here,  $v_{xc}^a$  is given by Eq. (30). All higher-order KS matrices contain only a Coulomb and an xc part. The Coulomb part is the same as in TDHF theory. Using the notation established above for the xc part, we can give the general formula for the higher-order KS matrices,

$$F_s^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n) = D^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n) \times (2J) + v_{xc}^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n), \quad (36)$$

where the frequencies  $\omega_a, \omega_b, \dots, \omega_n$  are equal to zero or  $\pm \omega$  in this work. The matrices  $v_{xc}^{ab \dots n}(\omega_a, \omega_b, \dots, \omega_n)$  have been given in Eq. (30) for first- and second-order. The higher-order results can straightforwardly be obtained from the results in the previous sections.

## VI. SOLVING THE NONLINEAR RESPONSE EQUATIONS USING THE $(2n+1)$ -THEOREM

Now that we have established the form of the higher-order KS matrices in DFT, we can continue with the solution of the (nonlinear) response equations. First, we will give an outline of how the equations are derived and after that, how they are solved efficiently. One starts by inserting the Taylor expansions for  $F_s$ ,  $C$ ,  $\varepsilon$ , and  $D$  in the time-dependent KS equations [Eq. (8)], the normalization condition [Eq. (9)], and expression for the density matrix [Eq. (10)]. Equating expressions on the left- and right-hand sides of these equations with the same time-dependence leads to the higher-order coupled equations. Up to third-order, these have been written out by Karna and Dupuis in Tables II, III, and IV of Ref. 17. For example, the first-order time-dependent KS equations can be written as

$$F_s^a(\omega)C^{(0)} + F_s^{(0)}C^a(\omega) + \omega S^{(0)}C^a(\omega) = S^{(0)}C^a(\omega)\varepsilon^{(0)} + S^{(0)}C^{(0)}\varepsilon^a(\omega), \quad (37)$$

where  $\omega=0$  for the static first-order equations and can be equal to either  $\omega$  or  $-\omega$  in the frequency-dependent case. As the higher-order expressions become rather lengthy and the DFT equations are identical to the TDHF equations, because the explicit form of the Fock or KS operator is not yet required, we will not repeat those expressions, and simply refer to Tables II, III, and IV of Ref. 17.

In order to calculate the desired NLO properties, one needs to solve the TDKS equations iteratively up to a certain order  $n$ , each time using the solutions to the lower-order equations. As a start, the static KS equations are solved, resulting in the matrices  $F_s^{(0)}$ ,  $C^{(0)}$ ,  $\varepsilon^{(0)}$ , and  $D^{(0)}$ , which yields the converged SCF density  $\rho^{(0)}$ . These matrices are

needed for the solution of the first-order KS equations, which yields the first-order density matrix, from which the frequency-dependent polarizability is immediately obtained through Eq. (19). We have previously described<sup>9</sup> how this first-order density can be obtained in an efficient, iterative  $N^3$  process, by making use of auxiliary basis function techniques, which are also often used for speeding up ordinary (zeroth-order) DFT calculations.

After the first-order equations have been solved, all the ingredients for an iterative solution of the second-order equations are available, which can be solved with the same techniques as the first-order equations. After the second-order equations are solved, the second-order density matrix is available, from which the frequency-dependent hyperpolarizability tensor is obtained through Eq. (19). This process can be repeated to arbitrary order, giving access to  $\gamma_{abcd}(-\omega_\sigma; \omega_b, \omega_c, \omega_d)$  and even higher-order hyperpolarizability tensors. However, this will require many iterative calculations if the full hyperpolarizability tensors are required (all possible combinations for  $a, b, c, d$ ) for different optical processes (different combinations of frequencies  $\omega_b, \omega_c, \omega_d$ ).

A more efficient approach is obtained from the use of the  $(2n+1)$ -theorem. It can be shown that for the calculation of the frequency-dependent first hyperpolarizability tensors  $\beta$ , only first-order quantities are needed.<sup>17</sup> Similarly, the calculation of  $\gamma$  and  $\delta$  (the third hyperpolarizability tensor) requires the knowledge of second-order quantities only. For example, only nine first-order response equations need to be solved in order to obtain all components  $abc$  of the first hyperpolarizability tensors  $\beta$  governing SHG [ $\beta_{abc}(-2\omega; \omega, \omega)$ ], EOPE [ $\beta_{abc}(-\omega; \omega, 0)$ ], optical rectification (OR) [ $\beta_{abc}(0; \omega, -\omega)$ ] and the static hyperpolarizability [ $\beta(0; 0, 0)$ ]. If the  $(2n+1)$ -theorem would not be used, the self-consistent solution of 27 second-order equations would be required in the most general case. If only the first hyperpolarizability tensor governing static effects is needed, the solution of only three first-order equations suffices.

After the first-order equations have been solved, the first hyperpolarizability tensors are obtained from a series of matrix multiplications, which do not contribute significantly to the required computing time. A practical consideration is that less programming effort is needed for the implementation of the  $(2n+1)$  equations, as only low-order response equations have to be solved. This explains the desirability of obtaining equations for  $\beta$  in terms of first-order quantities only. Karna and Dupuis have presented equations for all  $\beta$  and  $\gamma$  tensors which govern optical effects involving fields of frequency  $\omega$  and frequency 0, in which the  $(2n+1)$ -theorem has been used. For the important SHG and THG cases, they also give a step-by-step derivation of these results for the TDHF case. The DFT results can be obtained by following those steps. Here we will discuss the SHG case, for which an eight step algorithm is given by Karna and Dupuis (pp. 494–495 of Ref. 17). As the first seven steps do not use the explicit form of the Fock or KS matrices, the DFT equations remain identical to the TDHF equations, until the final step. After the first seven steps for the SHG case, we have



$$\begin{aligned}
& C^{a\dagger} (+2\omega) F^{bc} (\omega, \omega) C^0 + C^{a\dagger} (+2\omega) F^b (\omega) C^c (\omega) + C^{a\dagger} (+2\omega) F^c (\omega) C^b (\omega) + C^{a\dagger} (+2\omega) F^0 C^{bc} (\omega, \omega) \\
& + 2\omega C^{a\dagger} (+2\omega) S^0 C^{bc} (\omega, \omega) - C^{0\dagger} F^a (-2\omega) C^{bc} (+\omega, +\omega) - C^{a\dagger} (+2\omega) F^0 C^{bc} (+\omega, +\omega) \\
& - 2\omega C^{a\dagger} (+2\omega) S^0 C^{bc} (+\omega, +\omega) + C^{0\dagger} F^{bc} (+\omega, +\omega) C^a (-2\omega) + C^{c\dagger} (-\omega) F^b (+\omega) C^a (-2\omega) \\
& + C^{b\dagger} (-\omega) F^c (+\omega) C^a (-2\omega) + C^{bc\dagger} (-\omega, -\omega) F^0 C^a (-2\omega) - 2\omega C^{bc\dagger} (-\omega, -\omega) S^0 C^a (-2\omega) \\
& - C^{bc\dagger} (-\omega, -\omega) F^a (-2\omega) C^0 - C^{bc\dagger} (-\omega, -\omega) F^0 C^a (-2\omega) + 2\omega C^{bc\dagger} (-\omega, -\omega) S^0 C^a (-2\omega) \\
& = C^{a\dagger} (+2\omega) S^0 C^{bc} (\omega, \omega) \varepsilon^0 + C^{a\dagger} (+2\omega) S^0 C^b (\omega) \varepsilon^c (\omega) + C^{a\dagger} (+2\omega) S^0 C^c (\omega) \varepsilon^b (\omega) \\
& + C^{a\dagger} (+2\omega) S^0 C^0 \varepsilon^{bc} (\omega, \omega) - \varepsilon^0 C^{a\dagger} (+2\omega) S^0 C^{bc} (+\omega, +\omega) - \varepsilon^{a\dagger} (+2\omega) C^{0\dagger} S^0 C^{bc} (+\omega, +\omega) \\
& + \varepsilon^0 C^{bc\dagger} (-\omega, -\omega) S^0 C^a (-2\omega) + \varepsilon^c (+\omega) C^{b\dagger} (-\omega) S^0 C^a (-2\omega) + \varepsilon^b (+\omega) C^{c\dagger} (-\omega) S^0 C^a (-2\omega) \\
& + \varepsilon^{bc} (+\omega, +\omega) C^{0\dagger} S^0 C^a (-2\omega) - C^{bc\dagger} (-\omega, -\omega) S^0 C^a (-2\omega) \varepsilon^0 - C^{bc\dagger} (-\omega, -\omega) S^0 C^0 \varepsilon^a (-2\omega). \quad (38)
\end{aligned}$$

In the final step, the goal is to end up with an equation of the form

$$\begin{aligned}
\beta_{abc}(-2\omega; \omega, \omega) &= -\text{Tr} [H^a D^{bc}(\omega, \omega)] \\
&= \text{Tr} [\text{first-order quantities}]. \quad (39)
\end{aligned}$$

This is achieved by multiplying Eq. (38) on both sides with the occupation number matrix  $n$  and taking the trace. One furthermore adds the quantity  $\text{Tr} [n\{C^{b\dagger}(-\omega)F^a(-2\omega)C^c(+\omega) + C^{c\dagger}(-\omega)F^{a\dagger}(+2\omega)C^b(+\omega)\}]$  to both sides of the equation.<sup>17</sup> While some second-order terms cancel in a trivial way, others can be removed by using the property of the trace operator that  $\text{Tr} [ABC] = \text{Tr} [CAB]$ , the fact that  $n$  is a diagonal matrix and the properties of the  $\varepsilon$  Lagrangian matrices.<sup>17</sup> One furthermore rewrites the equation in terms of the second-order density matrix and the dipole moment matrix, in order to obtain a result of the form of Eq. (39).

All this proceeds in exactly the same way in the DFT and TDHF cases. The remaining term which needs to be removed contains the second-order Fock or KS matrix. This term is of the form

$$\text{Tr} [-F_s^a(-2\omega)D^{bc}(+\omega, +\omega) + D^a(-2\omega)F_s^{bc}(+\omega, +\omega)]. \quad (40)$$

Using the DFT expressions for the first and second-order KS matrices, this can be rewritten to

$$\begin{aligned}
& \text{Tr} [-F_s^a(-2\omega)D^{bc}(+\omega, +\omega) + D^a(-2\omega)F_s^{bc}(+\omega, +\omega)] \\
& = -\text{Tr} [H^a D^{bc}(+\omega, +\omega) + D^a(-2\omega) \times (2J^0) D^{bc}(+\omega, \\
& +\omega) + f_{xc}(2\omega) D^a(-2\omega) D^{bc}(+\omega, +\omega) \\
& - D^a(-2\omega) D^{bc}(+\omega, +\omega) \times (2J^0) - D^a(-2\omega) \\
& \times (f_{xc}(2\omega) D^{bc}(\omega, \omega) + g_{xc}(\omega, \omega) D^b(\omega) D^c(\omega))] \\
& = -\text{Tr} [H^a D^{bc}(+\omega, +\omega) - g_{xc}(\omega, \omega) D^a \\
& \times (-2\omega) D^b(\omega) D^c(\omega)]. \quad (41)
\end{aligned}$$

Here, Eq. (30) has been used for the xc terms. The second term on the right-hand side of Eq. (41) is an additional term in the DFT expression for  $\beta(-2\omega; \omega, \omega)$ , not present in the TDHF case, which is due to the nonlinearity of  $v_{xc}$  in terms of the density. Repeating this procedure for the other processes yields a general expression for the extra terms

$$\begin{aligned}
[\beta^{\text{DFT}}]_{abc}(-\omega_\sigma; \omega_b, \omega_c) &= [\beta^{\text{HF}}]_{abc}(-\omega_\sigma; \omega_b, \omega_c) \\
&+ \text{Tr}[g_{xc}(\omega_b, \omega_c) D^a(-\omega_\sigma) \\
&\times D^b(\omega_b) D^c(\omega_c)]. \quad (42)
\end{aligned}$$

These equations are very schematic in the sense that the rest of the  $(2n+1)$ -expression for  $\beta$  is equal in form only for the DFT and HF cases. Explicit expressions are given below, and can also be found in Table VII of Ref. 17. The final term (the extra DFT term) is most efficiently calculated through a numerical integration

$$\begin{aligned}
& \text{Tr} [g_{xc}(\omega_b, \omega_c) D^a(-\omega_\sigma) D^b(\omega_b) D^c(\omega_c)] \\
& = \int d^3\mathbf{r} \int d^3\mathbf{r}' \int d^3\mathbf{r}'' g_{xc}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_b, \omega_c) \\
& \times \rho^a(\mathbf{r}, -\omega_\sigma) \rho^b(\mathbf{r}', \omega_b) \rho^c(\mathbf{r}'', \omega_c). \quad (43)
\end{aligned}$$

This numerical integration looks quite expensive, but, in the usual approximation to  $g_{xc}$  (see following section), it becomes trivial as it reduces to a single, instead of triple, integral. For the static case, the extra DFT term was already obtained by Fournier,<sup>38</sup> and by Colwell *et al.*,<sup>33</sup> while Kormornicki and Fitzgerald<sup>39</sup> have also considered the efficient evaluation of similar terms.

## VII. APPROXIMATIONS USED IN DFT RESPONSE CALCULATIONS

Although the density functional formalism for the treatment of frequency-dependent NLO response is exact in principle, practical calculations require approximations to the unknown xc functionals. The functionals which have to be approximated are the usual xc potential  $v_{xc}(\mathbf{r})$ , which is needed in the zeroth-order KS equations, and its functional derivatives  $f_{xc}$ ,  $g_{xc}$ , and so on. For  $v_{xc}(\mathbf{r})$ , which is the functional derivative of the xc energy functional  $E_{xc}$  with respect to the (time-independent) density, many approximations exist. The most usual ones are those based upon the local density approximation (LDA), for example in the Vosko–Wilk–Nusair (VWN) parametrization,<sup>40</sup> or the potentials based on the generalized gradient approximations (GGAs), such as the exchange functional by Becke,<sup>41</sup> and the Perdew<sup>42</sup> or Lee–Yang–Parr<sup>43</sup> correlation functionals.

The xc potential determines the zeroth-order KS orbitals and their one-electron energies. It is consequently clear that the quality of the xc potential is of the utmost importance for the hyperpolarizability results. In fact, the usual potentials mentioned above are not the most suitable ones for response calculations as they decay exponentially, whereas the correct decay should be Coulombic. It has been shown several times<sup>44,45</sup> that potentials which do possess the correct asymptotic behavior provide significantly more accurate results than the LDA or GGA potentials. The choice of the xc potential hardly influences the time needed in the response calculation, as it is needed in the solution of the usual KS equations only. After that, only the resulting orbitals and one-electron energies are needed.

The xc kernels are more complicated functionals than the xc potential. Whereas the xc potential depends upon  $\mathbf{r}$  only,  $g_{xc}$ , for example, depends upon the spatial variables  $\mathbf{r}, \mathbf{r}'$ , and  $\mathbf{r}''$  and the frequency variables  $\omega_b$  and  $\omega_c$ . Very little is known about the xc kernels  $f_{xc}$  and  $g_{xc}$ . Because of the lack of more refined approximations as well as for efficiency reasons, one has usually employed very simple approximations to these kernels in the practical calculations until now. Although a frequency-dependent model for  $f_{xc}$  exists (the Gross–Kohn kernel<sup>46–48</sup>), such a model is not available for the higher-order kernels. Furthermore, the Gross–Kohn kernel exhibits some undesired properties. As a consequence, in virtually all molecular applications of time-dependent density functional response theory, the so-called adiabatic approximation has been invoked. The term adiabatic is used because the time-dependent xc potential is assumed to depend in the same way on the time-dependent density as the static xc potential depends upon the time-independent density, which is a good approximation for slow (adiabatic) processes. A direct consequence of this approximation is that the frequency-independent versions of the xc kernels are used,

$$f_{xc}^{\text{adiabatic}}(\mathbf{r}, \mathbf{r}', \omega) = f_{xc}(\mathbf{r}, \mathbf{r}', \omega = 0), \quad (44)$$

$$g_{xc}^{\text{adiabatic}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_a, \omega_b) = g_{xc}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_a = 0, \omega_b = 0).$$

This approximation is justified for small  $\omega$ -values, but it appears to work well even outside this domain. At the moment, it remains unclear whether or not the adiabatic approximation is a severe one. If one uses the functional derivative of the LDA potential, in combination with the adiabatic approximation, one obtains the simple ALDA kernels, which are local in space as well,

$$\begin{aligned} f_{xc}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', \omega) &= f_{xc}^{\text{hom}}(\mathbf{r}, \mathbf{r}', \omega = 0) \delta(\mathbf{r} - \mathbf{r}') \\ g_{xc}^{\text{ALDA}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_a, \omega_b) &= g_{xc}^{\text{hom}}(\mathbf{r}, \mathbf{r}', \mathbf{r}'', \omega_a = 0, \omega_b = 0) \delta(\mathbf{r} - \mathbf{r}') \delta(\mathbf{r} - \mathbf{r}''). \end{aligned} \quad (45)$$

Here, we have added the specification “hom” to the kernel in order to specify that this approximation is based upon the homogeneous electron gas. The spatial locality of the ALDA kernels ensures the computational efficiency of the DFT response calculations. If a model is used in which the spatial nonlocality of the kernels is taken into account (as for ex-

ample in the  $f_{xc}$ -kernel based upon the time-dependent optimized effective potential (TDOEP) in the exchange-only approximation<sup>49</sup>), this efficiency is lost to a great extent. This is due to the fact that six-dimensional numerical integrations will have to be performed for  $f_{xc}$  and nine-dimensional numerical integrations for  $g_{xc}$ . In the ALDA, only three-dimensional numerical integrations are required, due to the delta functions in Eq. (45).

At present, there are no models for  $f_{xc}$  which clearly improve upon the ALDA, although such models will likely appear in the future. For this reason, the ALDA seems the most logical choice for the moment. If more refined approximations for  $f_{xc}$  and  $g_{xc}$  will appear in the future, a compromise between accuracy and efficiency will be required. Numerical evidence for atoms and small molecules<sup>50</sup> suggests however that the major approximation made in the response calculations is usually due to the xc potential, and not to its functional derivatives. Our hyperpolarizability results for small molecules<sup>15</sup> suggest furthermore that  $g_{xc}$  has only a small influence on the final  $\beta$ -values (at least in the ALDA). As a nonlocal model for  $g_{xc}$  will enormously increase the computational cost of the calculations, this will probably not be worthwhile for a long time. The influence of the chosen model for  $f_{xc}$  on  $\beta$  is larger.

## VIII. IMPLEMENTATION

In this section we are concerned with the question what the most efficient implementation of the DFT equations for the frequency-dependent hyperpolarizabilities should look like. As we have described our implementation for the solution of the linear response equations previously,<sup>9</sup> we will be mainly concerned with the hyperpolarizabilities here, but we will discuss the most important points of the linear response calculations. Using Karna and Dupuis' notation, where  $G$  stands for the Fock/KS matrix on eigenfunction basis, we can write for the first-order KS matrix  $G_s^a$ ,

$$\begin{aligned} [G_s^a(\omega)]_{pq} &= \int d\mathbf{r} \phi_p(\mathbf{r}) [\mu_a E^a(\mathbf{r}, \omega) \\ &\quad + v_{\text{Coul}}^a(\mathbf{r}) + v_{xc}^a(\mathbf{r})] \phi_q(\mathbf{r}). \end{aligned} \quad (46)$$

All matrix elements of this type, whether they are on eigenfunction basis or on AO basis, are determined by numerical integration, because the complicated xc term makes an analytical evaluation impossible.

As the KS matrix  $G_s$  depends upon the first-order density matrix, through the potential terms  $v_{\text{Coul}}^a(\mathbf{r})$  and  $v_{xc}^a(\mathbf{r})$ , a self-consistent solution is required, as the first-order density matrix in its turn is determined by the first-order KS matrix. In our implementation, this iterative process can be performed either in the AO basis or in the eigenfunction basis. For very large systems, the AO option has the advantage that integral prescreening and more general linear scaling techniques<sup>14</sup> can be applied. This would result in a drastic reduction of the number of integrals which have to be calculated and in the cost per integral, since the parts of space which do not contribute to a certain integral can be excluded from the numerical integration. As in the solution of the ordinary KS equations, such techniques will in the future

result in a solution of the linear response equations which scales linearly with the number of atoms.

However, for medium-sized and highly symmetric systems, the eigenfunction basis is preferred, as only matrix elements between occupied and virtual orbitals are required, and as symmetry can be used straightforwardly to further reduce the number of numerical integrations. Because one needs substantial basis sets for an accurate hyperpolarizability calculation, the number of occupied orbitals times the number of virtual orbitals may be substantially less than  $N*(N+1)/2$ , where  $N$  is the number of (primitive) AOs. As the linear scaling techniques have not yet been implemented, the eigenfunction option is the default one in our implementation. The Coulomb potential of the first-order density in Eq. (46) is obtained from a fitted density  $\tilde{\rho}^{(1)}$ , reducing the cost of the solution of the KS equations and the linear response equations from  $N^4$  to  $N^3$ .<sup>9</sup>

The most demanding hyperpolarizability calculation for  $\beta$  is one where all components of  $\beta$  for all optical effects considered in this work are required. In such a case, the linear response equations need to be solved at frequencies  $0, \omega$  and  $2\omega$ , with external fields in the  $x, y$ , and  $z$  directions. The converged first-order KS matrices are passed to the part of the code for calculating the first hyperpolarizabilities. Although only the occupied-virtual block of the first-order KS matrix is needed in a linear response calculation, the occupied-occupied and virtual-virtual blocks are also generated (from the converged first-order density matrix), because they are necessary for the nonlinear response calculations. From the KS matrices, all other first-order information can be regenerated. For example, the first-order transformation matrices  $U^a(\omega_a)$ , defined by<sup>17</sup>

$$C^{(0)}U^a(\omega_a) = C^a(\omega_a) \quad (47)$$

are, with a suitable (nondiagonal!) choice for the Lagrangian multiplier matrices,<sup>17</sup> given by

$$[U^a(\omega_a)]_{pq} = \frac{[G_s^a(\omega_a)]_{pq}}{\varepsilon_q^{(0)} - \varepsilon_p^{(0)} - \omega_a}, \quad (48)$$

where  $\varepsilon_q^{(0)}$  and  $\varepsilon_p^{(0)}$  are the KS one-electron energies and where  $U$  is nonzero only for the occupied-virtual blocks. This choice for the  $\varepsilon$ -matrix represents what Gonze<sup>28</sup> calls the parallel-transport gauge. An alternative choice is to take a diagonal Lagrangian multiplier matrix  $\varepsilon$ , the diagonal gauge.<sup>28</sup> Certain technical problems which have to be addressed in the diagonal gauge, are absent in the parallel-transport gauge, such as the fact that the occupied-occupied block of the  $U$ -matrix is no longer zero. In this block, divergent terms may appear if  $\varepsilon_q^{(0)} = \varepsilon_p^{(0)}$  and  $\omega = 0$ . For this reason, most practical implementations use the parallel-transport gauge,<sup>17,28</sup> in which the first-order Lagrangian matrices  $\varepsilon^a$  are block-diagonal and given by

$$[\varepsilon^a(\omega_a)]_{pq} = [G_s^a(\omega_a)]_{pq}, \quad (49)$$

where  $p$  and  $q$  are both occupied or both virtual.

The equations of the previous section can be used to obtain the DFT expressions for the first hyperpolarizability tensors. Using the fact that the diagonal parts of the first-

order Fock matrices in Table VII of Ref. 17 are equal to the diagonal blocks of the first-order Lagrangian multiplier matrices  $\varepsilon$  [Eq. (49)], we obtain the following compact  $(2n+1)$ -expressions for the DFT frequency-dependent hyperpolarizabilities  $\beta_{abc}(-\omega_\sigma; \omega_b, \omega_c)$ ,

$$\begin{aligned} \beta_{abc}(-\omega_\sigma; \omega_b, \omega_c) &= \text{Tr} \{ n U^a(-\omega_\sigma) [G_s^b(\omega_b), U^c(\omega_c)]_- \} \\ &+ \text{all permutations of } (a, -\omega_\sigma), (b, \omega_b), (c, \omega_c) \\ &+ \text{Tr} [g_{xc}(\omega_b, \omega_c) D^a(-\omega_\sigma) D^b(\omega_b) D^c(\omega_c)], \end{aligned} \quad (50)$$

where  $[\cdot]_-$  stands for the ordinary commutator and where the final term is the extra term of the DFT equations. In this work, the frequencies  $\omega_b$  and  $\omega_c$  are assumed to be equal to zero or  $\omega$ , but Eq. (50) is valid for general frequencies.

It should be clear from the above that the work which is needed for the calculation of the first hyperpolarizability tensors  $\beta$  is determined by the time needed for the solution of the linear response equations (9 linear response equations in the worst case). Afterwards, a few matrix multiplications suffice for the determination of all discussed  $\beta$  tensors. One can use the form of these matrices [for example the fact that the matrices are block-off-diagonal ( $U$ ) or diagonal ( $n$ )] to further reduce the work done in these matrix multiplications, but this is not the time-determining factor in the calculation.

The term which is extra in the DFT expression for  $\beta$  [the final term in Eq. (50)] should be treated carefully. One should not calculate the term in the form in which it is given in Eq. (50). That would require evaluating all matrix elements  $[g_{xc}]_{\kappa\lambda\mu\nu\sigma\tau}$  in Eq. (31), which would be very expensive. Instead one should numerically evaluate the integral in Eq. (43),<sup>38</sup> which, with the ALDA kernel, reduces to

$$\int d^3\mathbf{r} g_{xc}^{\text{ALDA}}(\mathbf{r}) \rho^a(\mathbf{r}, -\omega_\sigma) \rho^b(\mathbf{r}, \omega_b) \rho^c(\mathbf{r}, \omega_c). \quad (51)$$

The numerical evaluation of this integral requires a negligible amount of computer time,<sup>38</sup> but extreme care is needed in its evaluation. This can be seen from the asymptotic behavior of  $g_{xc}^{\text{ALDA}}$ . This kernel behaves as  $\rho^{-5/3}$ , implying that it diverges at infinity. This is counterbalanced by the first-order densities, which go to zero in an exponential fashion. This requires an accurate first-order density in the outer region of the molecule. The fitted first-order density displays certain anomalies in the outer region where the density is low, such as small oscillations around the exact density. For this reason, the exact (not fitted) first-order densities are calculated in the integration points and stored. Similarly, the xc kernels are calculated using the exact zero-order density  $\rho^{(0)}$ . Regions where the zero-order density is below a certain threshold are not taken into account, in order to prevent the occurrence of numerical problems in the evaluation of the integral. Similar remarks about the evaluation of this term were made by Lee and Colwell<sup>34</sup> for the static case.

## IX. TESTS ON THE IMPLEMENTATION AND DISCUSSION OF EFFECTS OF A FINITE AUXILIARY BASIS SET

The equations for the various hyperpolarizability tensors which have been derived in the previous sections hold rigor-

TABLE I. Test calculation on the  $\gamma_{zzzz}$  second hyperpolarizability component of helium, calculated from  $\beta_{zzz}$  values at  $E_1^z=0.001$ . All quantities in a.u.

Method	$E_1^z, E_2^z$	$\gamma_{zzzz}$ (0;0,0,0) <sup>a</sup>	$\gamma_{zzzz}$ (- $\omega$ ; $\omega$ ,0,0) <sup>a,b</sup>
FF from $\alpha_{zz}$	0.001, 0.00025	87.915	89.359
FF from $\alpha_{zz}$	0.001, 0.00050	87.9163	89.3605
FF from $\alpha_{zz}$	0.001, 0.00100	87.9164	89.3595
FF from $\beta_{zzz}$	0.001, analytic	87.9163	89.3595

<sup>a</sup> $\gamma_{zzzz}$  obtained from  $\beta_{zzz}$  at  $E_1^z=0.001$  a.u., where  $\beta_{zzz}$  was calculated either analytically or from Eq. (52).

<sup>b</sup>Tensor related to the electro-optical Kerr effect (EOKE), at  $\omega=0.05$  a.u.

ously if one does not use a density fit, or if the set of auxiliary basis functions (fit functions) is complete. In our implementation we have assumed that these results also hold to a good approximation for finite but large auxiliary basis sets. For example, we make the approximation that Eq. (41) is valid for fitted densities as well. Similar approximations were made by Fournier<sup>38</sup> when considering static perturbations. Although taking the finiteness of the fit set into account would in principle be possible and desirable, it would lead to considerable extra programming effort. Fournier, Andzelm and Salahub<sup>51</sup> have considered the analytic calculation of first-order derivatives in the presence of a fit. Second derivatives have been considered by both Dunlap and Andzelm<sup>52</sup> and by Komornicki and Fitzgerald,<sup>39</sup> while Fournier<sup>38</sup> has considered both second and third derivatives in the presence of a density fit. All these authors consider time-independent properties only, but their work could still be followed to a large extent in order to obtain expressions where the fit approximation has been explicitly taken into account. In the ADF program the situation will be somewhat different from the case considered in these papers, as the density is fitted directly and not the potential due to this density.

It should be emphasized at this point that our aim here is primarily to document the technical accuracy of our implementation. We have previously shown that our implementation can be applied to molecules of the size of C<sub>60</sub>,<sup>10</sup>

TABLE II. Influence of finite auxiliary basis set on the static hyperpolarizability of CO.

Fit set	Density used for $v_{xc}$	Method	$\beta_{zzx}$ (a.u.)	$\beta_{zzz}$ (a.u.)
large <sup>a</sup>	fitted	analytic	-8.239	-33.522
large	fitted	finite field <sup>b</sup>	-8.274	-33.588
large	fitted	finite field <sup>c</sup>	-8.275	-33.593
large	exact	analytic	-8.433	-33.900
large	exact	finite field <sup>b</sup>	-8.440	-33.901
medium <sup>d</sup>	fitted	analytic	-7.054	-31.023
medium	fitted	finite field <sup>b</sup>	-7.573	-33.421

<sup>a</sup>The large fit set consists of 254 STO fit functions per atom. See text.

<sup>b</sup>Using  $E_2=0.0005$  a.u. in Eq. (52).

<sup>c</sup>Using  $E_2=0.001$  a.u. in Eq. (52).

<sup>d</sup>The medium-sized fit set consists of 184 STO fit functions per atom. See text.

TABLE III. Static and frequency-dependent average hyperpolarizabilities of para-nitroaniline at  $\lambda=1060$  nm ( $\omega=0.043$  a.u.).

Property	LDA/ALDA <sup>a</sup>	LB94/ALDA <sup>a</sup>	HF <sup>b</sup>	MP2 <sup>c</sup>
$\beta_{\text{vec}}(0;0,0)$ <sup>d</sup>	14.89	16.28	4.37	8.55
$\beta_{\text{vec}}(-2\omega;\omega,\omega)$ <sup>d</sup>	33.97	42.31	4.88	12.0
$\bar{\gamma}(0;0,0,0)$ <sup>e</sup>	7.34	2.62	1.48	3.21
$\bar{\gamma}(-2\omega;\omega,\omega,0)$ <sup>e</sup>	20.18	11.98	2.11	4.6

<sup>a</sup>This work, using ALDA for functional derivatives of  $v_{xc}$ , and either LDA or LB94 for  $v_{xc}$  itself.

<sup>b</sup>Reference 58.

<sup>c</sup>Results obtained by Sim *et al.* (Ref. 54), frequency dispersion was estimated from the TDHF calculation.

<sup>d</sup> $\beta_{\text{vec}}=\beta_z=(1/3)\Sigma_a\beta_{zaa}+\beta_{aza}+\beta_{aaz}$ , given in units of  $10^{-30}$  esu, as in Refs. 58,60,54.

<sup>e</sup> $\bar{\gamma}=(1/15)\Sigma_{a,b}(2\gamma_{aabb}+\gamma_{abba})$ , in  $10^{-36}$  esu, as in Ref. 58.

for which  $\gamma_{zzzz}(0;0,0,0)$ ,  $\gamma_{zzzz}(-\omega;\omega,0,0)$  and  $\gamma_{zzzz}(-2\omega;\omega,\omega,0)$  were calculated for a range of frequencies. A calibration study on a set of small molecules, in which the appropriateness of several xc potentials is tested, and in which both static and frequency-dependent first and second hyperpolarizabilities are treated, is reported separately,<sup>15</sup> as is a further application of our implementation to large polyene chains.<sup>53</sup>

Here, we will show that for (very) large basis and fit sets, the results from analytic calculations of  $\beta$  and finite difference calculations with respect to the polarizability in various small electric fields, are in fact identical. Tests are performed on He and CO in large basis sets (Tables I and II) and on para-nitroaniline in a standard basis (Table III). For helium we calculate  $\gamma_{zzzz}$  from  $\gamma_{zzzz}(-\omega;\omega,0,0)\approx 1000\times\beta_{zzz}(-\omega;\omega,0)|_{E_1^z=0.001}$ , where  $\beta_{zzz}$  is either calculated analytically, or from the FF differentiation of  $\alpha_{zz}(-\omega;\omega)$  at  $E=E_1^z\pm E_2^z$  and  $E=E_1^z\pm 2E_2^z$ ,<sup>54</sup>

$$\beta_{zzz}^{\text{FF}}(-\omega;\omega,0)|_{E=E_1^z} = \frac{1}{E_2^z} \left[ \frac{2}{3} [\alpha_{zz}(-\omega;\omega)|_{E=E_1^z+E_2^z} - \alpha_{zz}(-\omega;\omega)|_{E=E_1^z-E_2^z}] - \frac{1}{12} [\alpha_{zz}(-\omega;\omega)|_{E=E_1^z+2E_2^z} - \alpha_{zz}(-\omega;\omega)|_{E=E_1^z-2E_2^z}] \right], \quad (52)$$

where  $\beta^{\text{FF}}$  stands for the FF approximation to  $\beta$ , and where  $\alpha$  is obtained analytically from the solution of the first-order KS equations. Although we are aware that  $\gamma_{zzzz}$  can be obtained more directly and efficiently from  $\alpha$ , we use the present approach because it provides a more direct test of our implementation. Our static LDA (Ref. 40) result of  $\gamma_{zzzz}=\gamma=87.9$  a.u. (which, in view of the huge basis and fit sets we used, should be close to the basis set limit) is too large by roughly a factor of 2.<sup>55</sup>

This is expected from the well-known deficiencies of the LDA approximation, and better results can be obtained with asymptotically correct xc potentials such as the Van Leeuwen-Baerends (LB94) potential.<sup>56</sup> However, as we

have only implemented the ALDA for the xc kernels  $f_{xc}$  and  $g_{xc}$ , we can only perform “mixed” calculations with the LB94 potential, in which  $f_{xc}$  is not the functional derivative of  $v_{xc}$ . This implies that we cannot test the LB94 results with FF calculations, and that renders them useless for our present purpose of testing the implementation. In another work,<sup>15</sup> the quality of different xc potentials for hyperpolarizability calculations will be established. The results from the finite difference calculations for Helium are compared to the analytical result in Table I, for various field strengths  $E_2^z$ . Both the static hyperpolarizability result and the EOKE result at  $\omega=0.05$  a.u. agree very well with the finite difference results, proving the correctness of the implementation for these effects.

In Table II, we show our analytic and finite difference results [obtained from equations similar to Eq. (52) but at zero field:  $E=0$ ] for the hyperpolarizability of CO. Here, we investigate the effects of using a finite auxiliary basis set. The basis set which has been used is quite large and gives results close to the basis set limit, as shown by a comparison of our most accurate results to those obtained in a basis set free manner by Dickson and Becke.<sup>57</sup> With a FF LDA calculation, they obtain  $-33.7$  and  $-8.6$  for  $\beta_{zzz}$  and  $\beta_{zxx}$ , respectively, where we find  $-33.90$  and  $-8.44$ . In the first three rows of Table II, the analytic and finite difference results for the two independent components  $\beta_{zxx}$  and  $\beta_{zzz}$  of the static hyperpolarizability tensor of CO are compared. In these calculations, the fitted density was used for the evaluation of the (zeroth-order) xc potential in the solution of the KS equations. In the response equations, the xc terms are evaluated from the exact (not the fitted) density. It is clear that the agreement between the analytic and FF values is acceptable, in view of the sensitivity of this property, but not completely satisfactory. The deviations are 0.4% and 0.2%. If the xc potential is evaluated from the exact density (as shown in the fourth and fifth rows) the agreement between the finite difference and analytic results increases considerably. The deviations have reduced to 0.1% and 0.003%. A more important observation is that these results differ significantly from the results with an xc potential obtained from a fitted density. This shows that accuracy is required in all parts of the calculation if reliable hyperpolarizability results are required.

This becomes even clearer from the results in the final two rows, obtained in the same way as those from the first three rows, but with a medium-sized instead of a large fit set. (The large fit set consists of 13s, 11p, 10d, 10f, and 8g functions, giving a total of 254 STO auxiliary basis functions per atom. The medium-sized fit set consists of 8s, 7p, 6d, 7f, and 6g basis functions, which yields a total of 184 functions. This is to be compared with the basis set which consists of 4s, 3p, 1d, and 1f functions to which we added diffuse functions: 2s, 2p, 2d, and 2f functions.) The analytic results differ in the order of 10% from the results in the first rows, showing that a large auxiliary basis is needed for a reliable analytic determination of hyperpolarizabilities of small systems. Furthermore, the deviations between the FF and analytic results have increased enormously. The differences are no less than 7.4% and 7.7%. This implies that in the results with a

medium-sized fit set, the difference between a FF calculation and an analytic calculation is not negligible anymore. However, even in the FF case, a large fit set is required for high reliability.

Our final example is the para-nitroaniline molecule, in which we investigate the accuracy which can be reached for a medium-sized molecule in a standard valence triple zeta basis with two polarization functions, the largest standard basis in ADF. There is a large interest in this molecule,<sup>58–60,54,61</sup> which we study in the BLYP (Refs. 41,43)-optimized planar C(2v) geometry, due to its large hyperpolarizability  $\beta$  of which the zzz-component is the dominating part. As in Ref. 62, we have tested our implementation for the SHG tensor by checking if the dispersion formula (Refs. 63,55, and references therein)

$$\beta_{zzz}(-\omega_\sigma; \omega_b, \omega_c) = \beta_{zzz}(0; 0, 0) \times (1 + A_{zzz}(\omega_\sigma^2 + \omega_b^2 + \omega_c^2) + \dots), \quad (53)$$

relating the frequency dependencies of the various NLO effects, holds in our case, if a normal basis set is used.

From a fit to our  $\beta_{zzz}(-\omega; \omega, 0)$  results at six frequencies from 0 to 0.005 a.u., we obtain  $A_{zzz} = 54.845$  a.u., in excellent agreement with the value  $A_{zzz} = 54.842$  a.u. from the analytic  $\beta_{zzz}(-2\omega; \omega, \omega)$  results, which provides a strong indication for the correctness of our implementation for the SHG tensor. If we calculate  $\beta_{zzz}(-\omega; \omega, 0)$  from a FF calculation on  $\alpha_{zz}(-\omega; \omega)$  we obtain  $\beta_{zzz}(0; 0, 0) = -1959$  a.u. and  $A_{zzz} = 54.7$  a.u. both within 1% of the analytic result, which is very satisfactory as it shows that even standard basis and fit sets can be sufficiently accurate for large molecules.

We have gathered our LDA and LB94 results for the first and second average hyperpolarizabilities in Table III, to which *ab initio* HF and MP2 values have been added for the sake of comparison. Experimental values are available (for example in 1,4-dioxane (Ref. 64)), but these are not directly comparable to the gas phase theoretical values. Both the  $\beta(-2\omega; \omega, \omega)$  and  $\gamma(-2\omega; \omega, \omega, 0)$  results are clearly larger in comparison to previous *ab initio* studies.<sup>58–60,54</sup> The static results as well as the frequency dependence are substantially higher than in those papers, which we attribute to the position of the all-important amino-to-nitro excitation energy, for which our LDA value of 3.41 eV is too low for the gas phase.<sup>64</sup>

A basis set study of our results falls outside of the scope of the present work, but due to the dominance of the amino-to-nitro excitation, we believe our values for  $\beta$  to be reliable, as the addition of diffuse functions is known to have a limited effect for this system.<sup>54</sup> For the second hyperpolarizability, the neglect of diffuse functions could be more important.

Although a basis set study would be needed in order to study the difference between the LDA and LB94 results for  $\gamma$  in detail, the different treatment of the outer region of the molecule is the most probable cause of the large difference.

Our test calculations in which the numerical integration accuracy was varied indicate that demanding 5 accurate digits for a set of test integrals is generally sufficient for con-

verged results, while the default value of 4 is sufficient for standard cases. Finally, we note that in other applications to large molecules, like polyene chains,<sup>53</sup> the effects of using a modest basis and fit set are seen to be acceptable. There, the use of the small standard double-zeta STO basis set in ADF with the accompanying standard fit sets gave satisfactory agreement with FF calculations, in comparison to the results for CO and para-nitroaniline shown here. We therefore conclude that the use of auxiliary basis functions ("the fit set") and the numerical integrations are additional sources of errors, which can however be kept under control.

## X. SUMMARY AND OUTLOOK

In this work, we have derived the equations which are needed for calculating frequency-dependent hyperpolarizabilities using time-dependent DFT. The efficiency and accuracy of our computer implementation has been discussed, as well as the connection to related work. In particular, the differences with the closely-related TDHF approach have been emphasized. In a similar manner, the equations can be extended to higher-order hyperpolarizabilities. In previous and future applications, the implementation has been shown to be applicable to large systems. An application of the present work to a set of small molecules, in which the reliability of various density functionals will be assessed, is forthcoming.

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